

PATENT COOPERATION TREATY

EO/US
PCT/JP99/07144

PCT

NOTIFICATION OF ELECTION

(PCT Rule 61.2)

From the INTERNATIONAL BUREAU

To:

Assistant Commissioner for Patents
United States Patent and Trademark
Office
Box PCT
Washington, D.C.20231
ETATS-UNIS D'AMERIQUE

in its capacity as elected Office

Date of mailing: 27 July 2000 (27.07.00)	
International application No.: PCT/JP99/07144	Applicant's or agent's file reference: YCT-444
International filing date: 20 December 1999 (20.12.99)	Priority date: 21 January 1999 (21.01.99)
Applicant: MCCRAY, B., Scott et al	

1. The designated Office is hereby notified of its election made:

☒ in the demand filed with the International preliminary Examining Authority on:
25 April 2000 (25.04.00)

☐ in a notice effecting later election filed with the International Bureau on:

2. The election ☒ was
☐ was not

made before the expiration of 19 months from the priority date or, where Rule 32 applies, within the time limit under Rule 32.2(b).

The International Bureau of WIPO 34, chemin des Colombettes 1211 Geneva 20, Switzerland	Authorized officer: J. Zahra
Facsimile No.: (41-22) 740.14.35	Telephone No.: (41-22) 338.83.38

2000.12.-4

DIY.

From the
INTERNATIONAL PRELIMINARY EXAMINING AUTHORITY

PCT

To:

HOSOKAWA, Shinya
YUASA AND HARA
Section 206, New Ohtemachi Bldg,
2-1 Ohtemachi 2-chome
Chiyoda-ku
Tokyo 100-0004
JAPON

NOTIFICATION OF TRANSMITTAL OF
THE INTERNATIONAL PRELIMINARY
EXAMINATION REPORT
(PCT Rule 71.1)

Date of mailing
(day/month/year) 30.11.2000

Applicant's or agent's file reference
YCT-444

IMPORTANT NOTIFICATION

International application No.
PCT/JP99/07144

International filing date (day/month/year)
20/12/1999

Priority date (day/month/year)
21/01/1999

Applicant
EBARA CORPORATION et al.

1. The applicant is hereby notified that this International Preliminary Examining Authority transmits herewith the international preliminary examination report and its annexes, if any, established on the international application.
2. A copy of the report and its annexes, if any, is being transmitted to the International Bureau for communication to all the elected Offices.
3. Where required by any of the elected Offices, the International Bureau will prepare an English translation of the report (but not of any annexes) and will transmit such translation to those Offices.

4. REMINDER

The applicant must enter the national phase before each elected Office by performing certain acts (filing translations and paying national fees) within 30 months from the priority date (or later in some Offices) (Article 39(1)) (see also the reminder sent by the International Bureau with Form PCT/IB/301).

Where a translation of the international application must be furnished to an elected Office, that translation must contain a translation of any annexes to the international preliminary examination report. It is the applicant's responsibility to prepare and furnish such translation directly to each elected Office concerned.

For further details on the applicable time limits and requirements of the elected Offices, see Volume II of the PCT Applicant's Guide.

Name and mailing address of the IPEA/

 European Patent Office
D-80298 Munich
Tel. +49 89 2399 - 0 Tx: 523656 epmu d
Fax: +49 89 2399 - 4465

Authorized officer

Ipinazar, P

Tel. +49 89 2399-8131



PATENT COOPERATION TREATY

PCT

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Article 36 and Rule 70)

Applicant's or agent's file reference YCT-444	FOR FURTHER ACTION		See Notification of Transmittal of International Preliminary Examination Report (Form PCT/IPEA/416)
International application No. PCT/JP99/07144	International filing date (<i>day/month/year</i>) 20/12/1999	Priority date (<i>day/month/year</i>) 21/01/1999	
International Patent Classification (IPC) or national classification and IPC B01D69/08			
Applicant EBARA CORPORATION et al.			

1. This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.

2. This REPORT consists of a total of 6 sheets, including this cover sheet.

☒ This report is also accompanied by ANNEXES, i.e. sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).

These annexes consist of a total of 3 sheets.

3. This report contains indications relating to the following items:

- | | | |
|------|-------------------------------------|---|
| I | <input checked="" type="checkbox"/> | Basis of the report |
| II | <input type="checkbox"/> | Priority |
| III | <input type="checkbox"/> | Non-establishment of opinion with regard to novelty, inventive step and industrial applicability |
| IV | <input type="checkbox"/> | Lack of unity of invention |
| V | <input checked="" type="checkbox"/> | Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement |
| VI | <input type="checkbox"/> | Certain documents cited |
| VII | <input checked="" type="checkbox"/> | Certain defects in the international application |
| VIII | <input checked="" type="checkbox"/> | Certain observations on the international application |

Date of submission of the demand 25/04/2000	Date of completion of this report 30.11.2000
Name and mailing address of the international preliminary examining authority: <div style="display: flex; align-items: center;"> <div> European Patent Office D-80298 Munich Tel. +49 89 2399 - 0 Tx: 523656 epmu d Fax: +49 89 2399 - 4465 </div> </div>	Authorized officer Sembritzki, T Telephone No. +49 89 2399 8626



INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No. PCT/JP99/07144

I. Basis of the report

1. This report has been drawn on the basis of *(substitute sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to the report since they do not contain amendments (Rules 70.16 and 70.17).):*

Description, pages:

1-5,7-11,13-24	as originally filed		
6,12	as received on	17/11/2000	with letter of 17/11/2000

Claims, No.:

1-18,19 (part)	as originally filed		
19 (part),20-24	as received on	17/11/2000	with letter of 17/11/2000

2. With regard to the **language**, all the elements marked above were available or furnished to this Authority in the language in which the international application was filed, unless otherwise indicated under this item.

These elements were available or furnished to this Authority in the following language: , which is:

- ☐ the language of a translation furnished for the purposes of the international search (under Rule 23.1(b)).
- ☐ the language of publication of the international application (under Rule 48.3(b)).
- ☐ the language of a translation furnished for the purposes of international preliminary examination (under Rule 55.2 and/or 55.3).

3. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international preliminary examination was carried out on the basis of the sequence listing:

- ☐ contained in the international application in written form.
- ☐ filed together with the international application in computer readable form.
- ☐ furnished subsequently to this Authority in written form.
- ☐ furnished subsequently to this Authority in computer readable form.
- ☐ The statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.
- ☐ The statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished.

4. The amendments have resulted in the cancellation of:

- ☐ the description, pages:
- ☒ the claims, Nos.: 23
- ☐ the drawings, sheets:

**INTERNATIONAL PRELIMINARY
EXAMINATION REPORT**

International application No. PCT/JP99/07144

5. ☐ This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed (Rule 70.2(c)):

(Any replacement sheet containing such amendments must be referred to under item 1 and annexed to this report.)

6. Additional observations, if necessary:

V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement

Novelty (N)	Yes: Claims 1-22, 24
	No: Claims
Inventive step (IS)	Yes: Claims 1-22, 24
	No: Claims
Industrial applicability (IA)	Yes: Claims 1-22, 24
	No: Claims

- 2. Citations and explanations**
see separate sheet

VII. Certain defects in the international application

The following defects in the form or contents of the international application have been noted:
see separate sheet

VIII. Certain observations on the international application

The following observations on the clarity of the claims, description, and drawings or on the question whether the claims are fully supported by the description, are made:
see separate sheet

Point V:

1. Novelty and inventive step

- 1.1 In claim 1 of the present application a process for the fabrication of a hollow fiber membrane is defined. The subject-matter of claim 1 comprises several process steps and the definition of the spinning solution. The process steps itself are well known from the prior art cited in the search report and from page 2, lines 1-3 of the present application, however, the subject-matter of claim 1 differs from the available prior art in that the amount of both, a low molecular weight pore-former and a high molecular weight pore-former used in the spinning solution are defined.

Accordingly, the subject-matter of claim 1 is novel (Article 33(2) PCT).

- 1.2 Due to the use of two different pore-formers the pore-size distribution within the wall structure is improved and the water flux is increased. Comparative examples with only one pore-former resulted in undesirably large voids or nonporous wall structures and no or only a low porosity of the outside surface.
The problem to be solved by the present invention may therefore be regarded as how to provide a durable hollow fiber membrane which has a high water flux. The solution to this problem proposed in claim 1 of the present application is neither known from nor suggested by the available prior art.

Accordingly, the subject-matter of claim 1 is considered as involving an inventive step (Article 33(3) PCT). The same argumentation is valid for the membrane (claim 15) which is produced by the process defined in the claims.

- 1.3 Claims 2-14 and 16-24 are dependent on claims 1 and 15 and as such also meet the requirements of the PCT with respect to novelty and inventive step.

2. Industrial application

The industrial applicability is obvious.

Point VII:

3. Certain defects

- 3.1 The independent claims are not in the two-part form in accordance with Rule 6.3(b) PCT, which in the present case would be appropriate, with those features known in combination from the prior art being placed in the preamble (Rule 6.3(b)(i) PCT) and with the remaining features being included in the characterising part (Rule 6.3(b)(ii) PCT).

The process steps b-e are already known from the prior art. Independent claims should therefore be redrafted accordingly. If, however, the applicant is of the opinion that the two-part form would be inappropriate, then reasons therefor should be provided in the letter of reply. In addition, the applicant should ensure that it is clear from the description which features of the subject-matter of the claims are already known in combination from the prior art (see the PCT Guidelines, III-2.3a).

Point VIII:

4. Clarity

- 4.1 The present set of claims is not in logical order, which renders the claims unclear (Article 6 PCT), product and process claims are mixed and should be separated. It is not understood, why in the present case more than two independent claims, one independent process claim and one independent product claim are necessary.

Although claims 18 and 19 are drafted as independent claims behind the product claims, they clearly represent special embodiments of the process defined in claims 1-14 and should therefore be redrafted as claims dependent on these claims.

- 4.2 Claims 15 and 24 are so-called "product by process" claims, which are only allowable, if the product itself cannot be defined by clear technical parameters. Since the definition of a "product by process" claim is only understood in the meaning of "product obtainable by a process", the product itself must be novel

**INTERNATIONAL PRELIMINARY
EXAMINATION REPORT - SEPARATE SHEET**

International application No. PCT/JP99/07144

and clearly distinguishable from other membranes. The definitions of claims 15 and 24 could therefore lead to problems within the regional or national phase.

- 4.3 The definition of claim 10 is contradictory to claim 1 (Article 6 PCT). The minimum weight ratio of the pore-formers to each other can only be 0,3333.. (5 divided by 15) and not 0,3 as defined in claim 10.
- 4.4 The difference between process steps g and h (claims 17 and 18) cannot be understood (Article 6 PCT).
- 4.5 The use of the term "preferably" on pages 4 and 5 is misleading and renders the claims unclear (Article 6 PCT). The concerned parameters are not preferred, but are essential to the process defined in claim 1.

PART 34 AMDT

of this water is preferably introduced to the spinning solution by reason of the addition of the spinning solution's other components since such other components are very hydrophilic and tend to have non-zero concentrations of absorbed water. Since the concentration of water in these other components will depend on the methods used to dry them prior to formulating the spinning solution, it is desirable to add a small amount of water to maintain a total water concentration of between about 0.05 and 1 wt%.

Suitable spinning solution solvents include dimethyl sulfoxide (DMSO), dimethylacetamide (DMAC), dimethylformamide (DMF), and N-methyl pyrrolidone (NMP).

To form the solution, all components should first be thoroughly dried. Then, the components are mixed at elevated temperature, generally 80°C to 100°C, for a suitable length of time, say, 16 to 48 hours. The resulting solution should be clear and have a viscosity ranging from about 30 to about 100 Pa.s (about 30,000 to about 100,000 cp) at 65°C. It should be noted that the components of these spinning solutions tend to precipitate when cooled, the temperature at which time the precipitation takes place being dependent upon the specific formulation of the spinning solution. Generally, precipitation takes place when the solutions are cooled below about 50°C. In some cases, the solution will cloud immediately prior to precipitation. It has been found that the solution can be cooled to the point of precipitation, then re-heated to greater than about 65°C so as to re-form

1. Preparation of the Spinning Solution. A spinning solution was prepared by dissolving 30 wt% EVAL copolymer containing 44 mol% ethylene (EVAL Co. of America, Lisle, Illinois), 8.5 wt% PEG having a molecular weight of 3350 Daltons, 8.5 wt% EG, and 0.13 wt% water in DMSO by mixing said components at 80°C for 16 hours. The resulting homogeneous solution had a viscosity of 50 Pa.s (50,000 cp) at 65°C. This solution was maintained at 65°C prior to spinning.

2. Spinning the Hollow Fiber. The so-formed spinning solution was extruded through the orifice of a needle-in-orifice spinneret. A lumen-forming solution of water was injected simultaneously through the needle. The tip of the needle was maintained about 1 cm above the quench bath.

3. Quenching and Rinsing. The spun fiber was formed into a hollow fiber membrane by drawing it into a quench bath whereupon it precipitated. The bath comprised 25 wt% IPA in water maintained at 50°C. The residence time in the quench bath was approximately 20 seconds. The fiber was then rinsed for about 15 minutes in a godet filled with water at 50°C, then stretched by a factor of 2.4, i.e., the take-up speed was 2.4 times faster than the godet speed, then taken up onto a drum and further rinsed in hot water maintained at 40°-50°C. The fibers were then removed from the drum and rinsed overnight in hot water maintained at 45°-50°C.

4. Drying. The fibers were removed from the overnight rinse and soaked in 100% IPA for 10 minutes and then in 100% hexane for an additional 10 minutes prior to drying at

18.

20. The process of claim 19 wherein said crosslinking is conducted by a process comprising the
5 steps:

- (i) soaking said hollow fiber membrane in an aqueous solution of glutaraldehyde;
- (ii) drying said hollow fiber membrane; and
- (iii) annealing said hollow fiber membrane.

10

21. The process of any one of claims 17-20 wherein, in the heat treating step (g) or (h), tension on the fiber is decreased to as close to zero as possible by using two pulleys and allowing the fiber to sag between these
15 pulleys.

20

22. The process of any one of claims 17-21 wherein, in the heat treating step (g) or (h), the hot water treatment temperature is not less than 80°C.

23. (cancelled)

24. The hollow fiber membrane product of the process of any one of claims 17-23.

PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau



79 1289553

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁷ : B01D 69/08, 71/38, 67/00	A1	(11) International Publication Number: WO 00/43115 (43) International Publication Date: 27 July 2000 (27.07.00)
(21) International Application Number: PCT/JP99/07144 (22) International Filing Date: 20 December 1999 (20.12.99) (30) Priority Data: 09/234,755 21 January 1999 (21.01.99) US (63) Related by Continuation (CON) or Continuation-in-Part (CIP) to Earlier Application US 09/234,755 (CIP) Filed on 21 January 1999 (21.01.99) (71) Applicant (for all designated States except US): EBARA CORPORATION [JP/JP]; 11-1, Haneda Asahi-cho, Ohta-ku, Tokyo 144-8510 (JP). (72) Inventors; and (75) Inventors/Applicants (for US only): MCCRAY, B., Scott [US/US]; 63415 Saddleback Place, Bend, OR 97701 (US). FRIESEN, T., Dwayne [US/US]; 60779 Currant, Bend, OR 97702 (US). SIDWELL, R., Delores [US/US]; 19072 Pumice Butte Road, Bend, OR 97702 (US). LYON, K., David [US/US]; 20448 Klahani Drive, Bend, OR 97702 (US). SAKASHITA, Daichi [JP/JP]; 7-8-20-101, Shonandai, Fujisawa-shi, Kanagawa 252-0804 (JP).		(74) Agent: HOSOKAWA, Shinya; Yuasa And Hara, Section 206, New Ohtemachi Bldg., 2-1, Ohtemachi 2-chome, Chiyoda-ku, Tokyo 100-0004 (JP). (81) Designated States: AU, CA, CN, JP, KR, SG, US, European patent (DE, FR, GB, IT, NL). Published <i>With international search report.</i>
(54) Title: ETHYLENE-VINYL ALCOHOL HOLLOW FIBER MEMBRANES		
(57) Abstract EVAL microporous hydrophilic hollow fiber membranes are formed from a casting dope that includes low and high molecular weight pore-formers. Post-fabrication treatment includes stretching, hot water soaking and crosslinking.		

INTERNATIONAL SEARCH REPORT

09/889553

International Application No

PCT/JP 99/07144

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 B01D69/08 B01D71/38 B01D67/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 B01D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 0 747 113 A (KURARAY CO) 11 December 1996 (1996-12-11) page 3, line 30 -page 4, line 17; example 7	1,4,5, 7-11,15
A	FR 2 314 215 A (KURARAY CO) 7 January 1977 (1977-01-07) page 3, line 16 -page 5, line 22 page 11, line 9 - line 3	1,4-6,9, 12,15, 17,23
A	US 3 907 675 A (CHAPURLAT ROBERT ET AL) 23 September 1975 (1975-09-23) column 3, line 7-14 -/-	1,9,13, 15,17,24

☒ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

* Special categories of cited documents:

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

- "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- "S" document member of the same patent family

Date of the actual completion of the international search

6 March 2000

Date of mailing of the international search report

14/03/2000

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Faria, C

INTERNATIONAL SEARCH REPORT

Intern. Appl. Application No

PCT/JP 99/07144

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	<p>PATENT ABSTRACTS OF JAPAN vol. 004, no. 182 (C-035), 16 December 1980 (1980-12-16) & JP 55 122010 A (KURARAY CO LTD), 19 September 1980 (1980-09-19) abstract</p>	<p>1,9,13, 15</p>

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/JP 99/07144

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
EP 0747113	A	11-12-1996	CN 1141233 A	29-01-1997
			JP 9052030 A	25-02-1997
			US 5789081 A	04-08-1998
			US 5976433 A	02-11-1999
FR 2314215	A	07-01-1977	JP 1222318 C	15-08-1984
			JP 52094361 A	08-08-1977
			JP 58056379 B	14-12-1983
			JP 51145474 A	14-12-1976
			CA 1073822 A	18-03-1980
			DE 2625681 A	17-03-1977
			GB 1503270 A	08-03-1978
			US 4134837 A	16-01-1979
US 3907675	A	23-09-1975	FR 2201911 A	03-05-1974
			FR 2233086 A	10-01-1975
			BE 802580 A	21-01-1974
			CA 1027721 A	14-03-1978
			CH 578027 A	30-07-1976
			DE 2337069 A	07-02-1974
			ES 417081 A	01-08-1975
			GB 1420988 A	14-01-1976
			IL 42801 A	30-04-1976
			IT 994997 B	20-10-1975
			JP 49091970 A	03-09-1974
			NL 7309747 A	22-01-1974
			ZA 7304954 A	26-06-1974
JP 55122010	A	19-09-1980	NONE	

PCTWORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁷ : B01D 69/08, 71/38, 67/00	A1	(11) International Publication Number: WO 00/43115 (43) International Publication Date: 27 July 2000 (27.07.00)
(21) International Application Number: PCT/JP99/07144 (22) International Filing Date: 20 December 1999 (20.12.99) (30) Priority Data: 09/234,755 21 January 1999 (21.01.99) US (63) Related by Continuation (CON) or Continuation-in-Part (CIP) to Earlier Application US 09/234,755 (CIP) Filed on 21 January 1999 (21.01.99) (71) Applicant (for all designated States except US): EBARA CORPORATION [JP/JP]; 11-1, Haneda Asahi-cho, Ohta-ku, Tokyo 144-8510 (JP). (72) Inventors; and (75) Inventors/Applicants (for US only): MCCRAY, B., Scott [US/US]; 63415 Saddleback Place, Bend, OR 97701 (US). FRIESEN, T., Dwayné [US/US]; 60779 Currant, Bend, OR 97702 (US). SIDWELL, R., Delores [US/US]; 19072 Pumice Butte Road, Bend, OR 97702 (US). LYON, K., David [US/US]; 20448 Klahani Drive, Bend, OR 97702 (US). SAKASHITA, Daichi [JP/JP]; 7-8-20-101, Shonandai, Fujisawa-shi, Kanagawa 252-0804 (JP).		(74) Agent: HOSOKAWA, Shinya; Yuasa And Hara, Section 206, New Ohtemachi Bldg., 2-1, Ohtemachi 2-chome, Chiyoda-ku, Tokyo 100-0004 (JP). (81) Designated States: AU, CA, CN, JP, KR, SG, US, European patent (DE, FR, GB, IT, NL). Published <i>With international search report.</i>
(54) Title: ETHYLENE-VINYL ALCOHOL HOLLOW FIBER MEMBRANES (57) Abstract <p>EVAL microporous hydrophilic hollow fiber membranes are formed from a casting dope that includes low and high molecular weight pore-formers. Post-fabrication treatment includes stretching, hot water soaking and crosslinking.</p>		

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece	ML	Mali	TR	Turkey
BG	Bulgaria	HU	Hungary	MN	Mongolia	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MR	Mauritania	UA	Ukraine
BR	Brazil	IL	Israel	MW	Malawi	UG	Uganda
BY	Belarus	IS	Iceland	MX	Mexico	US	United States of America
CA	Canada	IT	Italy	NE	Niger	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NL	Netherlands	VN	Viet Nam
CG	Congo	KE	Kenya	NO	Norway	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NZ	New Zealand	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	PL	Poland		
CM	Cameroon	KR	Republic of Korea	PT	Portugal		
CN	China	KZ	Kazakstan	RO	Romania		
CU	Cuba	LC	Saint Lucia	RU	Russian Federation		
CZ	Czech Republic	LJ	Liechtenstein	SD	Sudan		
DE	Germany	LK	Sri Lanka	SE	Sweden		
DK	Denmark	LR	Liberia	SG	Singapore		
EE	Estonia						

DESCRIPTION

ETHYLENE-VINYL ALCOHOL HOLLOW FIBER MEMBRANES

5 BACKGROUND ART

Hollow fiber membranes have gained acceptance for use in treating many aqueous streams. In some cases, use of hollow fiber membranes is essential for the supply of clean drinking water and for treatment of wastewater. Hollow
10 fiber membranes can also be used to de-water sludges and other streams containing suspended solids. Key to the successful use of such membranes for these purposes is that the membrane be hydrophilic, allowing the membrane to "wet" when in contact with the stream to be treated. For this to
15 occur, the membrane should advantageously be made from a hydrophilic polymer.

One such polymer that has proved suitable for making hydrophilic hollow-fiber membranes is an ethylene-vinyl alcohol (EVAL) copolymer. Such a copolymer is known to be
20 useful in blood dialysis and, because of its hydrophilicity and excellent rejection of high molecular weight substances such as proteins, has many other uses in medical and laboratory applications. Typically, EVAL hollow fiber membranes are cast by forcing a solution of EVAL copolymer
25 through an orifice along with a lumen-forming solution and into a coagulation bath to form membranes having different morphologies and pore structures, depending upon the composition of the casting dope and the process conditions.

See, for example, U.S. Patent Nos. 4,134,837, 4,269,713, 4,317,729 4,362,677, 4,385,094, and Japanese Published Application No. 57-18924. Although a variety of these patents report the use of either a low molecular weight pore-former or a high molecular weight pore-former, there is no recognition of the value of a mixture of both low and high molecular weight pore-formers, and the EVAL membranes prepared according to the processes reported still suffer from a relatively low water flux and limited structural integrity and lifetime when used in applications requiring higher fluid pressures.

DISCLOSURE OF INVENTION

According to the present invention there is provided a process for the fabrication of a strong, durable microporous hydrophilic hollow fiber membrane having high water flux. The process comprises casting the membrane by conventional spinneret technology from a casting dope comprising an EVAL copolymer having a particular composition, followed by a series of post-casting steps.

The casting dope comprises EVAL copolymer in a solvent; a small amount of water; and two pore-formers, one low molecular weight and one high molecular weight. The lumen-forming fluid and the coagulation bath are of conventional composition. After precipitation or coagulation, the hollow fiber membranes are preferably stretched, soaked in hot water, and crosslinked.

BEST MODE FOR CARRYING OUT THE INVENTION

An ideal microporous hydrophilic hollow fiber membrane has three essential characteristics. First, the fiber should have a high water flux. Generally, water
5 fluxes greater than about $2 \text{ m}^3/\text{m}^2 \cdot \text{d} \cdot 0.1 \text{ MPa}$ at 25°C will lead to commercially practical processes. Second, the fiber should have a high wet tensile strength. This will ensure that the fiber has a long lifetime when operating under high pressure differentials, or when the fiber is
10 under stress during operation. Generally, the wet tensile strength of the fiber should be on the order of at least about 180 g/fil. Third, the fiber should have a high wet elongation at break so as to ensure long fiber lifetimes and durability under operating conditions. Generally, the
15 wet elongation at break should be greater than about 40%.

A microporous hydrophilic hollow fiber membrane with such characteristics will be useful for a wide range of applications, including water purification, wastewater treatment and dewatering sludges. The present invention
20 describes a process for the fabrication of such a membrane.

The first step in preparing a microporous hydrophilic hollow fiber membrane according to the present invention is to prepare a spinning solution, comprising a mixture of an EVAL copolymer, a low molecular weight pore-former, a
25 high molecular weight pore-former, water, and a solvent.

Although virtually any EVAL copolymer may be used in the present invention, copolymers with an ethylene content (relative to vinyl alcohol content) of 27 mol% to 48 mol%

are especially suitable.

In making a high-performance membrane, the concentration of EVAL copolymer in the spinning solution should be greater than about 25 wt% based upon the total weight of the spinning solution. If the concentration of copolymer is less than this, the strength of the resulting fiber is too low. Conversely, if the concentration of copolymer is too high, the water flux through the fiber is too low. It has been found that the concentration of EVAL copolymer should be kept in the range of 25 to 40 wt% to obtain practical water fluxes.

The spinning solution preferably contains at least two pore-formers: one with a low molecular weight and one with a high molecular weight. The term "low molecular weight" means ≤ 100 Daltons; and "high molecular weight" means ≥ 1000 Daltons. It has been found that this combination of pore-formers results in a structure suitable for a high-performance membrane. If only a low molecular weight pore-former is used, it has been found that the wall of the resulting fiber contains large voids. These voids reduce the strength of the fiber and are likely to result in defects or damage. In addition, use of only a low molecular weight pore-former leads to an outside surface with little or no porosity, which leads to low water fluxes. Conversely, if only a high molecular weight pore-former is used, it has been found that both the wall and the outside surface of the resulting fiber has low porosity, also leading to low water fluxes. Preferably, the

weight ratio of the low molecular weight pore-former to the high molecular weight pore-former should be greater than about 0.3 but less than about 3. The spinning solution preferably contains the low molecular weight pore-former and the high molecular weight pore-former in an amount of 5 to 15 wt%, respectively, based on the total weight of the spinning solution.

Virtually any low molecular weight pore-former may be used, provided that the compound is not a solvent for the EVAL copolymer and provided it is miscible with the other components of the spinning solution and with the quench baths. Exemplary classes of suitable low molecular weight pore-formers include alcohols, ketones, amines, and esters. It has been found that the most effective low molecular weight pore-formers are mono- and polyhydric alcohols, such as n-propanol, isopropanol (IPA), n-butanol, ethylene glycol (EG), and glycerol.

The high molecular weight pore-former preferably, is soluble in the solvent used to form the spinning solution and miscible in the spinning solution, resulting in solutions that are clear as opposed to cloudy. Exemplary suitable high molecular weight pore-formers include polyols such as polyethylene glycol (PEG), polypropylene glycol (PPG), and polyvinyl alcohol (PVA), polyvinyl pyrrolidone (PVP), and polyethylene oxide (PEO).

The spinning solution preferably also contains a small amount of water, in the order of 0.05 to 1 wt% based on the total weight of the spinning solution. The majority

of this water is preferably introduced to the spinning solution by reason of the addition of the spinning solution's other components since such other components are very hydrophilic and tend to have non-zero
5 concentrations of absorbed water. Since the concentration of water in these other components will depend on the methods used to dry them prior to formulating the spinning solution, it is desirable to add a small amount of water to maintain a total water concentration of between about
10 0.05 and 1 wt%.

Suitable spinning solution solvents include dimethyl sulfoxide (DMSO), dimethylacetamide (DMAC), dimethylformamide (DMF), and N-methyl pyrrolidone (NMP).

To form the solution, all components should first be
15 thoroughly dried. Then, the components are mixed at elevated temperature, generally 80°C to 100°C, for a suitable length of time, say, 16 to 48 hours. The resulting solution should be clear and have a viscosity ranging from about 30,000 to about 100,000 cp at 65°C. It should be noted
20 that the components of these spinning solutions tend to precipitate when cooled, the temperature at which time the precipitation takes place being dependent upon the specific formulation of the spinning solution. Generally, precipitation takes place when the solutions are cooled
25 below about 50°C. In some cases, the solution will cloud immediately prior to precipitation. It has been found that the solution can be cooled to the point of precipitation, then re-heated to greater than about 65°C so as to re-form

the spinning solution, with no adverse affects on the properties of fibers cast from the reconstituted solution. Preferably, however, the solution should be maintained at a temperature above the precipitation point (around $>50^{\circ}\text{C}$) while it is used, that is, while the solution is extruded to form a spun hollow fiber. In addition, the spinning solution should be filtered and degassed prior to casting hollow fiber membranes.

The membranes are cast by conventional spinneret technology, comprising extruding the spinning solution through the orifice of a needle-in-orifice spinneret. Simultaneously with the extrusion, a coagulating fluid is injected through the needle. Preferably, this coagulating fluid is an aqueous solution such as water alone or a mixture of water and a water-miscible organic fluid, generally characterized by the presence of at least 50 wt% water. Examples of suitable water-miscible organic fluids include low molecular weight alcohols, such as ethanol, IPA, n-propanol, EG and glycerol, and solvents used in the spinning solution, such as those mentioned above (DMSO, DMAC, NMP, and DMF).

From the spinneret, the extruded spinning solution and injected coagulating fluid are drawn into a quench bath consisting of 15 to 35 wt% alcohol in water. Exemplary alcohols include methanol, ethanol, IPA, n-propanol, butanol, EG, and propylene glycol. If the concentration of alcohol is less than about 15 wt%, the fiber quenches too rapidly, leading to a dense outside surface, and low water

fluxes. On the other hand, if the concentration of alcohol is too high, the fiber does not quench rapidly enough, leading to flattened or damaged fibers.

Prior to drawing the extruded spinning solution and
5 injected coagulating fluid into the quench bath, the same may be passed through an atmosphere. This atmosphere may consist of a gas, such as air or nitrogen, and may optionally contain a vapor, such as water vapor, solvent vapors, or other organic vapors. It has been found that
10 passing the extruded spinning solution and injected coagulating fluid through an atmosphere of ambient air for 0.05 to 0.1 second produces suitable fibers.

Another important variable in forming the hollow fiber is the temperature of the quench bath. It has been
15 found that the temperature should be maintained between about 40°C and about 65°C to form high-performance fibers. Generally, the higher the temperature of the quench bath, the larger is the resulting pore size on the outside surface of the membrane.

20 Once the microporous hollow fiber membrane has been formed, it should be rinsed to remove solvents and pore-formers, preferably with water. Generally, the water is maintained at a temperature of greater than about 40°C to ensure proper removal of the residual solvents and
25 pore-formers from the formed hollow fiber membrane. It has also been found that the performance of the fiber, and specifically, its water flux, can be increased by stretching the fiber during this rinsing step. Generally,

the degree of stretching should be such that the ratio of the length of the fiber after stretching to the length of the fiber prior to stretching is between about 1.3 and about 3.0.

5 Once the fiber has been rinsed, it is dried prior to use. In some cases, it is desirable to first rinse the fiber in IPA, then in hexane prior to drying to retain high performance of the fibers.

 The microporous hydrophilic hollow fiber membranes of
10 the present invention are also preferably crosslinked following fabrication. A particularly useful method for crosslinking the fibers involves the use of glutaraldehyde (GA), comprising (1) soaking the fiber in an aqueous GA solution, (2) drying the fiber, and (3) annealing the fiber.
15 In this procedure, the GA solution should be aqueous, and should contain a small amount of an inorganic acid such as HCl as a catalyst. The concentration of GA used in this crosslinking solution should generally be greater than about 0.1 wt% but less than about 5 wt%. The fibers should
20 be soaked in this solution for at least 1 minute, but less than 10 hours. The fiber should then be dried, usually at ambient temperature, to remove excess liquid solution. Drying times ranging from 1 minute to 4 hours have been found to be useful. The annealing step should be conducted
25 at a temperature greater than about 50°C, but less than about 120°C. The annealing step should be conducted for more than about 5 seconds, but less than about 6 hours.

 Another optional post-treatment which has been found

to increase the fiber's water flux is soaking the fiber in hot water (hot water treatment) after the rinsing step. The present inventors has found that membrane performance of the hydrophilic microporous hollow fiber membrane such as

5 flux and elongation at break may be significantly improved by subjecting the fiber to hot water treatment. The hot water treatment is conducted by soaking the prepared hydrophilic microporous hollow fiber membrane in a hot water bath at a temperature of 50° C to 100° C while relaxing

10 tension on the fiber. Relaxation of tension on the fiber in the hot water bath may be carried out by feeding the fiber in a hot water bath using two motorized pulleys, one pulley being used as an inlet pulley by which the fiber membrane is introduced into the bath, and the other pulley being used

15 as an outlet pulley by which the fiber membrane is pulled out from the bath, and maintaining the fiber placed in the bath in a "sagged" state between these two pulleys. It is important in this hot water treatment step for the fiber to be soaked in the hot water bath in fully sagged state,

20 preferably under substantially no tension, such that the fiber may be freely floating in water as if "swimming" in water. If the hot water treatment is carried out while tension is applied to the fiber membrane, flux cannot be improved by this treatment.

25 The hot water treatment may be carried out for a term of 1 second to 1 hour. This treatment will result in better effect when the fiber is sufficiently swelled with water prior to the treatment. The hot water treatment may improve

flux and elongation at break of the fiber membrane without affecting blocking ability or strength of the fiber membrane. The hot water treatment may be conducted just after the rinsing step as mentioned above. Or this hot water
5 treatment may be conducted on a fiber membrane after the fiber membrane is rinsed and dried, and even after being preserved for a long period of time, to improve mechanical properties of the fiber membrane. However, in order to accomplish significant improvement of membrane
10 performance, it is necessary to conduct the hot water treatment before the crosslinking step as mentioned above.

The thus heat treated hydrophilic microporous hollow fiber membrane may be taken up onto a drum. It is preferred that the fiber membrane is taken up onto a drum placed in
15 warm water at a temperature of 30°C to 70°C, and maintained therein for around one night. Thereafter, the fiber membrane taken up onto the drum in water may be preserved in cold water at a temperature of 10-20°C. By conducting such a post-treatment step, improved membrane performance
20 may be stabilized. When the crosslinking step is carried out after the hot water treatment, the fiber membrane preserved in cold water may be directly fed to the crosslinking step.

25

EXAMPLE 1

A microporous hydrophilic hollow-fiber membrane according to the present invention was fabricated using the following steps.

1. Preparation of the Spinning Solution. A

spinning solution was prepared by dissolving 30 wt% EVAL
copolymer containing 44 mol% ethylene (EVAL Co. of America,
Lisle, Illinois), 8.5 wt% PEG having a molecular weight of
5 3350 Daltons, 8.5 wt% EG, and 0.13 wt% water in DMSO by
mixing said components at 80° C for 16 hours. The resulting
homogeneous solution had a viscosity of 50,000 cp at 65° C.
This solution was maintained at 65° C prior to spinning.

2. Spinning the Hollow Fiber. The so-formed spinning
10 solution was extruded through the orifice of a needle-
in-orifice spinneret. A lumen-forming solution of water
was injected simultaneously through the needle. The tip of
the needle was maintained about 1 cm above the quench bath.

3. Quenching and Rinsing. The spun fiber was formed
15 into a hollow fiber membrane by drawing it into a quench
bath whereupon it precipitated. The bath comprised 25 wt%
IPA in water maintained at 50° C. The residence time in the
quench bath was approximately 20 seconds. The fiber was
then rinsed for about 15 minutes in a godet filled with
20 water at 50° C, then stretched by a factor of 2.4, i.e., the
take-up speed was 2.4 times faster than the godet speed,
then taken up onto a drum and further rinsed in hot water
maintained at 40° -50° C. The fibers were then removed from
the drum and rinsed overnight in hot water maintained at
25 45° -50° C.

4. Drying. The fibers were removed from the overnight
rinse and soaked in 100% IPA for 10 minutes and then in 100%
hexane for an additional 10 minutes prior to drying at

ambient temperature in a dry air stream.

The dried hollow-fiber membranes were examined under a scanning electron microscope (SEM). The inside diameter of the fibers was found to be 330 μm , while the outside diameter was 875 μm . The wall structure was seen to be highly porous, while the outside surface also exhibited a high porosity--both characteristics of high-performance membranes.

Samples of these fibers were then incorporated into a small test module and the outside of the fibers was pressurized to 0.3 MPa at ambient temperature, with filtered, deionized water. The water flux through the fibers was found to be outstanding at 10 $\text{m}^3/\text{m}^2 \cdot \text{d} \cdot 0.1 \text{ MPa}$ at 25°C. (The same units were used for measuring the fluxes of all hollow fiber membranes prepared in the Examples.)

Samples of the fibers were also soaked in water at ambient temperature for 1 hour and then tested for tensile strength. The wet tensile strength was found to be close to ideal, at 180 g/fil, while the wet elongation at break was excellent at 73%.

EXAMPLE 2

Post-fabrication crosslinking was performed as follows. Samples of the fibers from Example 1 were soaked in an aqueous solution of 1 wt% GA and 0.4 wt% HCl for 4 hours at room temperature. The fibers were then dried at ambient temperature for 2 hours prior to placing them in an oven for annealing. The temperature of the oven was

increased from ambient temperature to 80° C at a rate of 1° C /min, held at 80° C for 3 hours, and then cooled to ambient temperature over a period of 20 minutes. The properties of the resulting crosslinked fiber were measured following the procedures outlined in Example 1, and the results of the two presented in Table 1.

Table 1

Example No.	Water Flux (m ³ /m ² ·d·0.1 MPa)	Wet Tensile Strength (g/fil)	Wet Elongation Break (%)
1	10	180	73
2*	7.5	420	25

* crosslinked

10

EXAMPLES 3-6

The effects of stretching during rinsing the membranes of the present invention were studied. Microporous hydrophilic hollow fibers were prepared as in Example 1, except that the polymer solution comprised 33 wt% EVAL, 7.5 wt% PEG, 7.5 wt% EG, and 0.13 wt% water in DMSO, and the quench bath consisted of 30 wt% IPA in water. The degree of stretching ("stretch") during the rinse step was varied as shown in Table 2. These results show that if the degree of stretching is low, water flux is low. In addition, too much stretching results in low water fluxes and low elongations at break. Based on these results, the optimum degree of stretching appears to be 2.4.

20

Table 2

Example No.	Stretch	Water Flux ($\text{m}^3/\text{m}^2 \cdot \text{d} \cdot 0.1 \text{ MPa}$)	Wet Tensile Strength (g/fil)	Wet Elongation at Break (%)
3	1.0	0.0	140	230
4	1.8	4.5	120	90
5	2.4	10.0	130	51
6	3.0	1.0	150	42

EXAMPLES 7-10

The effect of the ratio of low molecular weight pore-former to high molecular weight pore-former was studied. Microporous hydrophilic hollow fiber membranes were prepared as in Example 1 except that various ratios of EG to PEG were used in the spinning solution. Samples of the so-cast fibers, together with samples of the fibers from Example 1 were examined by SEM. A summary of the observations from these examinations is presented in Table 3. Based upon the results, it was concluded that when the EG/PEG ratio is too low, the wall structure is nonporous and the outside surface has a low porosity. Conversely, if the EG/PEG ratio is too high, the wall structure has undesirably large voids and the outside surface has no porosity. Accordingly, it was concluded that a preferred range for the low molecular weight to high molecular weight pore-former ratio is from about 0.3 to about 3.0 to obtain a uniformly porous wall structure with a highly porous outside surface.

Table 3

Example No.	EG/PEG Ratio	Wall Structure	Outside Surface Structure
7	No EG	Nonporous	Low porosity
8	0.5	Uniformly porous	Moderate porosity
1	1	Uniformly porous	High porosity
9	3	Uniformly porous	Moderate porosity
10	no PEG	Large voids	No porosity

EXAMPLES 11-28

The effect of varying the crosslinking conditions on the wet tensile strength and wet elongation at break was studied. Microporous hydrophilic hollow fiber membranes were prepared as in Example 2, except that the conditions used for crosslinking the fibers were varied according to the values reported in Table 4, with the results shown in Table 4.

Table 4

Example No.	GA Conc. (Wt%)	Soak Time (min)	Oven Temp. Rate (OC/min)	Oven Temp (OC)	Time in Oven (hr)	Wet Tensile Strength (g/fil)	Wet Elongation at Break (%)
11	1	10	1	80	180	290	33
12	1	30	1	80	180	290	35
13	1	120	1	80	180	340	30
14	1	240	1	80	180	420	25
15	1	5	5	50	5	200	85
16	1	10	5	50	5	220	66
17	1	30	5	50	5	230	72
18	2.5	5	5	50	5	280	52
19	2.5	10	5	50	5	280	43
20	2.5	30	5	50	5	310	42
21	4	5	5	50	5	330	39
22	4	10	5	50	5	310	31
23	4	30	5	50	5	320	36
24	5	1	1	80	180	380	23
25	5	5	1	80	180	430	24
26	5	10	1	80	180	420	24
27	5	30	1	80	180	410	24
28	5	120	1	80	180	400	23

EXAMPLES 29-32

The effect of varying the temperature of the quench bath on flux was studied. Microporous hydrophilic hollow fiber membranes were prepared as in Example 1 except that the polymer solution comprised 32.5 wt% EVAL, 7.5 wt% PEG, 7.5 wt% EG, and 0.1 wt% water in DMSO, and the temperature of the quench bath was varied as indicated in Table 5, with the results shown in Table 5.

Table 5

Example No.	Quench Bath Temperature (° C)	Water Flux (m ³ /m ² ·d·0.1 MPa)
29	45	6.2
30	50	7.9
31	53	7.4
32	55	7.0

Examples 33-36

The effects of varying the temperature of the spinning
 5 solution was studied. Microporous hydrophilic hollow fiber
 membranes were prepared as in Examples 29-32 and the
 temperature of the spinning solution was varied as
 indicated in Table 6, with the results shown in Table 7.

Table 6

Example No.	Spinning Solution Temperature (° C)	Water Flux (m ³ /m ² ·d·0.1 MPa)
33	57	5.5
34	58	6.5
35	63	9.4
36	66	9.7

10

Examples 37-38

The following examples show the effect by conducting
 hot water treatment on the fiber membrane after rinsing or
 drying and before crosslinking.

15 A dry hollow fiber membrane obtained in Example 1 was
 preserved at room temperature for about one month. Thus
 preserved hollow fiber membrane was subjected to a hot
 water treatment in a hot water bath. Prior to the hot water
 treatment, the fiber was soaked in water at ambient
 20 temperature (around 20° C) to be swollen until the length

of the fiber is no longer changed. The fiber membrane was then soaked in a hot water bath maintained at 80°C for over one minute. During the hot water treatment, the fiber membrane placed in the hot water bath was maintained to be
5 sagged with no tension being applied thereto as if the fiber membrane was swimming in hot water. The thus treated fiber membrane was picked up from the bath and transferred into a water at ambient temperature (around 20°C) to cool the fiber membrane.

10 Water flux, wet tensile strength and wet elongation at break of the fiber membrane before and after the hot water treatment (HWT) as mentioned above were determined in a similar manner as in Example 1. The results are shown in Table 7 below as Example 37.

15 A hollow fiber membrane was formed and rinsed in a similar manner as in the steps (1)-(3) of Example 1. The thus obtained hollow fiber membrane just after rinsing step was subjected to a hot water treatment in a similar manner as mentioned above. Water flux, wet tensile strength and
20 wet elongation at break of the fiber membrane before and after the hot water treatment were determined in a similar manner as in Example 1. The results are shown in Table 7 as Example 38.

Table 7

Ex No	Clean Water Flux ($\text{m}^3/\text{m}^2 \cdot \text{d} \cdot 0.1 \text{ MPa}$)		Wet Tensile Strength (g/fil)		Wet Elongation at Break (%)	
	before HWT	after HWT	before HWT	after HWT	before HWT	after HWT
37	8.7	21.2	205	190	30	70
38	14.6	24.3	195	184	35	70

The results in Table 7 show that the hot water treatment according to the present invention improves water flux and wet elongation at break of the fiber membrane substantially without affecting tensile strength thereof, and this effect may be obtained either when the hot water treatment is conducted just after rinsing the fiber membrane or after drying and preserving it for a long period of time.

Examples 39-41

These examples show the effect of varying the hot water treatment time. Hydrophilic microporous hollow fiber membrane was prepared as in Example 38 except that the period of time for the fiber membrane to be soaked in the hot water bath (hot water treatment time) was varied. The results are shown in Table 8.

Table 8

Ex No	HWT time (seconds)	Clean Water Flux ($\text{m}^3/\text{m}^2 \cdot \text{d} \cdot 0.1 \text{ Mpa}$)	Wet Elongation at Break (%)
39	0	13.1	32
40	5	22.0	86
41	60	21.9	78

The results in Table 8 show that the hot water treatment according to the present invention improves water flux and elongation at break even when the hot water treatment time is as short as 5 seconds.

5

Examples 42-45

Reproducibility of the effect by the hot water treatment was examined. A hollow fiber membrane was formed and rinsed in a similar manner as in the steps (1)-(3) of Example 1. The thus obtained hollow fiber membrane just after rinsing step was subjected to a continuous hot water treatment as explained below. The fiber membrane was passed through the hot water bath maintained at 80°C for around 5 seconds. The hot water bath used in these examples was equipped with two motorized pulleys, one being used as a fiber membrane inlet pulley by which the fiber membrane is introduced into the bath, and the other being used as a fiber membrane outlet pulley by which the fiber membrane is pulled out from the bath. Using these two motorized pulleys, the fiber membrane placed in the hot water bath was maintained to be sagged with no tension being applied between the two pulleys as if the fiber membrane was swimming in hot water. The thus treated fiber membrane was taken up onto a drum placed in warm water at 50°C, and maintained therein over one night, and then dried at ambient temperature in a dry air stream.

The membrane performance after the hot water treatment of the thus obtained hydrophilic microporous

hollow fiber membrane are shown in Table 9.

Table 9

Ex No	Clean Water Flux ($\text{m}^3/\text{m}^2 \cdot \text{d} \cdot 0.1 \text{ Mpa}$)	Wet Tensile Strength (g/fil)	Wet Elongation at Break (%)
42	18.7	190	109
43	20.6	171	79
44	21.2	181	103
45	20.4	207	89

The results in Table 9 show that substantially
 5 equivalent effect are obtained in Examples 42-45, which
 reveals reproducibility of the effect by the hot water
 treatment according to the present invention.

Examples 46-47

10 The effect of the hot water treatment on blocking
 ability of the hollow fiber membrane was examined.
 According to the procedure of Example 38, two hydrophilic
 microporous hollow fiber membranes were prepared and
 subjected to the hot water treatment. Water flux and
 15 rejection of $0.1\mu\text{m}$ particles of the membranes before and
 after HWT were determined. The results are shown in Table
 10.

Table 10

Ex No	Clean Water Flux ($\text{m}^3/\text{m}^2 \cdot \text{d} \cdot 0.1 \text{ MPa}$)		Rejection of 0.1mm particles (%)	
	before HWT	after HWT	before HWT	after HWT
46	6.8	15.0	99	>99
47	7.8	16.4	99	99

20 The above results show that the hot water treatment

according to the present invention will not affect blocking ability of the hollow fiber membrane.

Examples 48-50

5 These examples show the effect of "relaxation" of fiber membrane during the hot water treatment. According to the procedure of Example 38, a hydrophilic microporous hollow fiber membrane was prepared. The fiber membrane was divided into three specimens and each of them was subjected
10 to the hot water treatment. In Example 48, the hot water treatment was carried out at 80°C for 1 minute while no tension was applied to the fiber membrane placed in the hot water bath. In Examples 49 and 50, the hot water treatment was carried out at 80°C for 1.5 minutes (Example 49) or 4
15 minutes (Example 50) while the fiber membrane placed in the hot water bath was strained by means of some pulleys placed in the hot water bath. Water flux and tensile properties before and after HWT were determined. The results are shown in Table 11.

20

Table 11

Ex No	Clean Water Flux (m ³ /m ² ·d·0.1 MPa)		Wet Tensile Strength (g/fil)		Wet Elongation at Break (%)	
	before HWT	after HWT	before HWT	after HWT	before HWT	after HWT
48	10.9	26.8	212	200	31	76
49	10.9	11.6	212	201	31	49
50	10.9	13.2	212	198	31	48

The results of Table 11 show that, if the hot water treatment is carried out while tension is applied to the

fiber membrane, flux and elongation at break of the fiber membrane is not improved.

5 The terms and expressions which have been employed in
the foregoing specification are used therein as terms of
description and not of limitation, and there is no
intention, in the use of such terms and expressions, of
excluding equivalents of the features shown and described
or portions thereof, it being recognized that the scope of
10 the invention is defined and limited only by the claims
which follow.

CLAIMS

1. A process for the fabrication of a microporous hydrophilic hollow fiber membrane from an ethylene-vinyl alcohol copolymer comprising the steps:

- 5 (a) providing a spinning solution comprising 25 to 40 wt% ethylene-vinyl alcohol copolymer, 5 to 15 wt% low molecular weight pore-former, 5 to 15 wt% high molecular weight pore-former, 0.05 to 1 wt% water, and a solvent;
- 10 (b) forming a spun hollow fiber by extruding said spinning solution through an orifice at a temperature above the precipitation point of the solution while simultaneously injecting a coagulating fluid through a needle located in said orifice;
- 15 (c) drawing said spun hollow fiber into a quench bath of 15 to 35 wt% of an alcohol in water at a temperature of 40° to 65° C to form a hydrophilic microporous hollow fiber membrane;
- 20 (d) rinsing said hydrophilic microporous hollow fiber membrane with water; and
- (e) drying said hydrophilic microporous hollow fiber membrane.

25

2. The process of claim 1 wherein said hollow fiber membrane is stretched during step (d).

3. The process of claim 2 wherein the degree of stretching during step (d) is from about 1.3 to about 3.0.

4. The process of claim 1 including an additional
5 step (f) comprising crosslinking said hollow fiber membrane.

5. The process of claim 4 wherein said crosslinking is conducted by a process comprising the steps:
10 (i) soaking said hollow fiber membrane in an aqueous solution of glutaraldehyde;
(ii) drying said hollow fiber membrane; and
(iii) annealing said hollow fiber membrane.

15 6. The process of claim 1 wherein the ethylene content of said ethylene-vinyl alcohol copolymer of step (a) is from 27 to 48 mol%.

7. The process of claim 1 wherein said low molecular
20 weight pore-former of step (a) is selected from monohydric and polyhydric alcohols.

8. The process of claim 1 wherein said high
molecular weight pore-former of step (a) is selected from
25 the group consisting of polyethylene glycol, polyethylene oxide, polypropylene glycol, polyvinylpyrrolidone and polyvinyl alcohol.

9. The process of claim 1 wherein said solvent of step (a) is selected from the group consisting of dimethylsulfoxide, dimethylformamide, dimethylacetamide, and N-methylpyrrolidone.

5

10. The process of claim 1 wherein the weight ratio of said low molecular weight pore-former to said high molecular weight pore-former of step (a) is from about 0.3 to about 3.

10

11. The process of claim 1 wherein said spinning solution of step (a) comprises 30 wt% ethylene-vinyl alcohol copolymer, 8.5 wt% ethylene glycol, 8.5 wt% polyethylene glycol, 0.1 wt% water and the solvent is dimethylsulfoxide.

15

12. The process of claim 1 wherein said coagulating fluid of step (b) is selected from the group consisting of water, mixtures of water and alcohols, mixtures of water and solvent, and mixtures of water, alcohols and solvent.

20

13. The process of claim 1 wherein said alcohol in step (c) is selected from the group consisting of methanol, ethanol, n-propanol, isopropanol, butanol, ethylene glycol and propylene glycol.

25

14. The process of claim 13 wherein said quench bath of step (c) comprises 20 to 30 wt% isopropanol in water.

15. The hollow fiber membrane product of the process of claim 1, 2 or 4.

5 16. The product of claim 15 wherein said hollow fiber membrane has a clean water flux greater than $2 \text{ m}^3/\text{m}^2 \cdot \text{d} \cdot 0.1 \text{ MPa}$ at 25°C , a wet tensile strength greater than about 180 g/fil, and a wet elongation at break greater than 40%.

10 17. The process of any one of claims 1-14 further comprising, after the rinsing step (d) and before the drying step (e), the step:

15 (g) subjecting the rinsed hydrophilic microporous hollow fiber membrane to hot water treatment in a hot water bath at a temperature of 50°C to 100°C while relaxing tension on the fiber.

18. A process for improving membrane performance of a microporous hydrophilic hollow fiber membrane comprising the step:

20 (h) subjecting the hydrophilic microporous hollow fiber membrane obtained by the process of any one of claims 1-3 and 6-14 to hot water treatment in a hot water bath at a temperature of 50°C to 100°C while relaxing tension on the fiber

25 19. A process for the fabrication of a microporous hydrophilic hollow fiber membrane comprising crosslinking a hollow fiber membrane obtained by the process of claim

18.

20. The process of claim 19 wherein said crosslinking is conducted by a process comprising the
5 steps:

- (i) soaking said hollow fiber membrane in an aqueous solution of glutaraldehyde;
- (ii) drying said hollow fiber membrane; and
- (iii) annealing said hollow fiber membrane.

10

21. The process of any one of claims 17-20 wherein, in the heat treating step (g) or (h), tension on the fiber is decreased to as close to zero as possible by using two pulleys and allowing the fiber to sag between these
15 pulleys.

22. The process of any one of claims 17-21 wherein, in the heat treating step (g) or (h), the hot water treatment temperature is not less than 80°C.

20

23. The process of any one of claims 17-22 wherein, in the taking up step (h) or (h), the hydrophilic microporous hollow fiber membrane taken up onto the drum is preserved in the water.

25

24. The hollow fiber membrane product of the process of any one of claims 17-23.

1. Preparation of the Spinning Solution. A

spinning solution was prepared by dissolving 30 wt% EVAL
copolymer containing 44 mol% ethylene (EVAL Co. of America,
Lisle, Illinois), 8.5 wt% PEG having a molecular weight of
5 3350 Daltons, 8.5 wt% EG, and 0.13 wt% water in DMSO by
mixing said components at 80° C for 16 hours. The resulting
homogeneous solution had a viscosity of 50,000 cp at 65° C.
This solution was maintained at 65° C prior to spinning.

2. Spinning the Hollow Fiber. The so-formed spinning
10 solution was extruded through the orifice of a needle-
in-orifice spinneret. A lumen-forming solution of water
was injected simultaneously through the needle. The tip of
the needle was maintained about 1 cm above the quench bath.

3. Quenching and Rinsing. The spun fiber was formed
15 into a hollow fiber membrane by drawing it into a quench
bath whereupon it precipitated. The bath comprised 25 wt%
IPA in water maintained at 50° C. The residence time in the
quench bath was approximately 20 seconds. The fiber was
then rinsed for about 15 minutes in a godet filled with
20 water at 50° C, then stretched by a factor of 2.4, i.e., the
take-up speed was 2.4 times faster than the godet speed,
then taken up onto a drum and further rinsed in hot water
maintained at 40° -50° C. The fibers were then removed from
the drum and rinsed overnight in hot water maintained at
25 45° -50° C.

4. Drying. The fibers were removed from the overnight
rinse and soaked in 100% IPA for 10 minutes and then in 100%
hexane for an additional 10 minutes prior to drying at

18.

20. The process of claim 19 wherein said crosslinking is conducted by a process comprising the
5 steps:

- (i) soaking said hollow fiber membrane in an aqueous solution of glutaraldehyde;
- (ii) drying said hollow fiber membrane; and
- (iii) annealing said hollow fiber membrane.

10

21. The process of any one of claims 17-20 wherein, in the heat treating step (g) or (h), tension on the fiber is decreased to as close to zero as possible by using two pulleys and allowing the fiber to sag between these
15 pulleys.

15

22. The process of any one of claims 17-21 wherein, in the heat treating step (g) or (h), the hot water treatment temperature is not less than 80°C.

20

23. The process of any one of claims 17-22 wherein, in the taking up step (h) or (h), the hydrophilic microporous hollow fiber membrane taken up onto the drum is preserved in the water.

25

24. The hollow fiber membrane product of the process of any one of claims 17-23.

PCT

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Article 36 and Rule 70)

Applicant's or agent's file reference YCT-444		FOR FURTHER ACTION See Notification of Transmittal of International Preliminary Examination Report (Form PCT/IPEA/416)
International application No. PCT/JP99/07144	International filing date (day/month/year) 20/12/1999	Priority date (day/month/year) 21/01/1999
International Patent Classification (IPC) or national classification and IPC B01D69/08		
Applicant EBARA CORPORATION et al.		

1. This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.



2. This REPORT consists of a total of 6 sheets, including this cover sheet.

☒ This report is also accompanied by ANNEXES, i.e. sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).

These annexes consist of a total of 3 sheets.

3. This report contains indications relating to the following items:

- I ☒ Basis of the report
- II ☐ Priority
- III ☐ Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
- IV ☐ Lack of unity of invention
- V ☒ Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
- VI ☐ Certain documents cited
- VII ☒ Certain defects in the international application
- VIII ☒ Certain observations on the international application

Date of submission of the demand 25/04/2000	Date of completion of this report 30.11.2000
Name and mailing address of the international preliminary examining authority:  European Patent Office D-80298 Munich Tel. +49 89 2399 - 0 Tx: 523656 epmu d Fax: +49 89 2399 - 4465	Authorized officer Sembritzki, T Telephone No. +49 89 2399 8626 

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No. PCT/JP99/07144

I. Basis of the report

1. This report has been drawn on the basis of *(substitute sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to the report since they do not contain amendments (Rules 70.16 and 70.17).):*

Description, pages:

1-5,7-11,13-24	as originally filed		
6,12	as received on	17/11/2000	with letter of 17/11/2000

Claims, No.:

1-18,19 (part)	as originally filed		
19 (part),20-24	as received on	17/11/2000	with letter of 17/11/2000

2. With regard to the **language**, all the elements marked above were available or furnished to this Authority in the language in which the international application was filed, unless otherwise indicated under this item.

These elements were available or furnished to this Authority in the following language: , which is:

- ☐ the language of a translation furnished for the purposes of the international search (under Rule 23.1(b)).
- ☐ the language of publication of the international application (under Rule 48.3(b)).
- ☐ the language of a translation furnished for the purposes of international preliminary examination (under Rule 55.2 and/or 55.3).

3. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international preliminary examination was carried out on the basis of the sequence listing:

- ☐ contained in the international application in written form.
- ☐ filed together with the international application in computer readable form.
- ☐ furnished subsequently to this Authority in written form.
- ☐ furnished subsequently to this Authority in computer readable form.
- ☐ The statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.
- ☐ The statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished.

4. The amendments have resulted in the cancellation of:

- ☐ the description, pages:
- ☒ the claims, Nos.: 23
- ☐ the drawings, sheets:

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No. PCT/JP99/07144

5. ☐ This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed (Rule 70.2(c)):

(Any replacement sheet containing such amendments must be referred to under item 1 and annexed to this report.)

6. Additional observations, if necessary:

V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement

Novelty (N)	Yes: Claims 1-22, 24
	No: Claims
Inventive step (IS)	Yes: Claims 1-22, 24
	No: Claims
Industrial applicability (IA)	Yes: Claims 1-22, 24
	No: Claims

2. Citations and explanations
see separate sheet

VII. Certain defects in the international application

The following defects in the form or contents of the international application have been noted:
see separate sheet

VIII. Certain observations on the international application

The following observations on the clarity of the claims, description, and drawings or on the question whether the claims are fully supported by the description, are made:
see separate sheet

Point V:

1. Novelty and inventive step

- 1.1 In claim 1 of the present application a process for the fabrication of a hollow fiber membrane is defined. The subject-matter of claim 1 comprises several process steps and the definition of the spinning solution. The process steps itself are well known from the prior art cited in the search report and from page 2, lines 1-3 of the present application, however, the subject-matter of claim 1 differs from the available prior art in that the amount of both, a low molecular weight pore-former and a high molecular weight pore-former used in the spinning solution are defined.

Accordingly, the subject-matter of claim 1 is novel (Article 33(2) PCT).

- 1.2 Due to the use of two different pore-formers the pore-size distribution within the wall structure is improved and the water flux is increased. Comparative examples with only one pore-former resulted in undesirably large voids or nonporous wall structures and no or only a low porosity of the outside surface.
- The problem to be solved by the present invention may therefore be regarded as how to provide a durable hollow fiber membrane which has a high water flux. The solution to this problem proposed in claim 1 of the present application is neither known from nor suggested by the available prior art.

Accordingly, the subject-matter of claim 1 is considered as involving an inventive step (Article 33(3) PCT). The same argumentation is valid for the membrane (claim 15) which is produced by the process defined in the claims.

- 1.3 Claims 2-14 and 16-24 are dependent on claims 1 and 15 and as such also meet the requirements of the PCT with respect to novelty and inventive step.

2. Industrial application

The industrial applicability is obvious.

Point VII:

3. Certain defects

- 3.1 The independent claims are not in the two-part form in accordance with Rule 6.3(b) PCT, which in the present case would be appropriate, with those features known in combination from the prior art being placed in the preamble (Rule 6.3(b)(i) PCT) and with the remaining features being included in the characterising part (Rule 6.3(b)(ii) PCT).

The process steps b-e are already known from the prior art. Independent claims should therefore be redrafted accordingly. If, however, the applicant is of the opinion that the two-part form would be inappropriate, then reasons therefor should be provided in the letter of reply. In addition, the applicant should ensure that it is clear from the description which features of the subject-matter of the claims are already known in combination from the prior art (see the PCT Guidelines, III-2.3a).

Point VIII:

4. Clarity

- 4.1 The present set of claims is not in logical order, which renders the claims unclear (Article 6 PCT), product and process claims are mixed and should be separated. It is not understood, why in the present case more than two independent claims, one independent process claim and one independent product claim are necessary.

Although claims 18 and 19 are drafted as independent claims behind the product claims, they clearly represent special embodiments of the process defined in claims 1-14 and should therefore be redrafted as claims dependent on these claims.

- 4.2 Claims 15 and 24 are so-called "product by process" claims, which are only allowable, if the product itself cannot be defined by clear technical parameters. Since the definition of a "product by process" claim is only understood in the meaning of "product obtainable by a process", the product itself must be novel

**INTERNATIONAL PRELIMINARY
EXAMINATION REPORT - SEPARATE SHEET**

International application No. PCT/JP99/07144

and clearly distinguishable from other membranes. The definitions of claims 15 and 24 could therefore lead to problems within the regional or national phase.

- 4.3 The definition of claim 10 is contradictory to claim 1 (Article 6 PCT). The minimum weight ratio of the pore-formers to each other can only be 0,3333.. (5 divided by 15) and not 0,3 as defined in claim 10.
- 4.4 The difference between process steps g and h (claims 17 and 18) cannot be understood (Article 6 PCT).
- 4.5 The use of the term "preferably" on pages 4 and 5 is misleading and renders the claims unclear (Article 6 PCT). The concerned parameters are not preferred, but are essential to the process defined in claim 1.

PCT

INTERNATIONAL SEARCH REPORT

(PCT Article 18 and Rules 43 and 44)

Applicant's or agent's file reference YCT-444	FOR FURTHER ACTION see Notification of Transmittal of International Search Report (Form PCT/ISA/220) as well as, where applicable, item 5 below.	
International application No. PCT/JP 99/07144	International filing date (day/month/year) 20/12/1999	(Earliest) Priority Date (day/month/year) 21/01/1999
Applicant EBARA CORPORATION et al.		

This International Search Report has been prepared by this International Searching Authority and is transmitted to the applicant according to Article 18. A copy is being transmitted to the International Bureau.

This International Search Report consists of a total of 3 sheets.

☒ It is also accompanied by a copy of each prior art document cited in this report.

1. Basis of the report

- a. With regard to the **language**, the international search was carried out on the basis of the international application in the language in which it was filed, unless otherwise indicated under this item.

☐ the international search was carried out on the basis of a translation of the international application furnished to this Authority (Rule 23.1(b)).

- b. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international search was carried out on the basis of the sequence listing :

☐ contained in the international application in written form.

☐ filed together with the international application in computer readable form.

☐ furnished subsequently to this Authority in written form.

☐ furnished subsequently to this Authority in computer readable form.

☐ the statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.

☐ the statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished

2. ☐ **Certain claims were found unsearchable** (See Box I).

3. ☐ **Unity of invention is lacking** (see Box II).

4. With regard to the **title**,

☒ the text is approved as submitted by the applicant.

☐ the text has been established by this Authority to read as follows:

5. With regard to the **abstract**,

☒ the text is approved as submitted by the applicant.

☐ the text has been established, according to Rule 38.2(b), by this Authority as it appears in Box III. The applicant may, within one month from the date of mailing of this international search report, submit comments to this Authority.

6. The figure of the **drawings** to be published with the abstract is Figure No.

☐ as suggested by the applicant.

☐ because the applicant failed to suggest a figure.

☐ because this figure better characterizes the invention.

☐ None of the figures.

of this water is preferably introduced to the spinning solution by reason of the addition of the spinning solution's other components since such other components are very hydrophilic and tend to have non-zero concentrations of absorbed water. Since the concentration of water in these other components will depend on the methods used to dry them prior to formulating the spinning solution, it is desirable to add a small amount of water to maintain a total water concentration of between about 0.05 and 1 wt%.

Suitable spinning solution solvents include dimethyl sulfoxide (DMSO), dimethylacetamide (DMAC), dimethylformamide (DMF), and N-methyl pyrrolidone (NMP).

To form the solution, all components should first be thoroughly dried. Then, the components are mixed at elevated temperature, generally 80° C to 100° C, for a suitable length of time, say, 16 to 48 hours. The resulting solution should be clear and have a viscosity ranging from about 30,000 to about 100,000 cp at 65° C. It should be noted that the components of these spinning solutions tend to precipitate when cooled, the temperature at which time the precipitation takes place being dependent upon the specific formulation of the spinning solution. Generally, precipitation takes place when the solutions are cooled below about 50° C. In some cases, the solution will cloud immediately prior to precipitation. It has been found that the solution can be cooled to the point of precipitation, then re-heated to greater than about 65° C so as to re-form

INTERNATIONAL SEARCH REPORT

International Application No

PCT/JP 99/07144

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 B01D69/08 B01D71/38 B01D67/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 B01D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 0 747 113 A (KURARAY CO) 11 December 1996 (1996-12-11) page 3, line 30 -page 4, line 17; example 7 ---	1,4,5, 7-11,15
A	FR 2 314 215 A (KURARAY CO) 7 January 1977 (1977-01-07) page 3, line 16 -page 5, line 22 page 11, line 9 - line 3 ---	1,4-6,9, 12,15, 17,23
A	US 3 907 675 A (CHAPURLAT ROBERT ET AL) 23 September 1975 (1975-09-23) column 3, line 7-14 --- -/--	1,9,13, 15,17,24

☒ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

° Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search

6 March 2000

Date of mailing of the international search report

14/03/2000

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Faria, C

INTERNATIONAL SEARCH REPORT

International Application No

PCT/JP 99/07144

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	<p>PATENT ABSTRACTS OF JAPAN vol. 004, no. 182 (C-035), 16 December 1980 (1980-12-16) & JP 55 122010 A (KURARAY CO LTD), 19 September 1980 (1980-09-19) abstract</p> <p>-----</p>	<p>1, 9, 13, 15</p>

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/JP 99/07144

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
EP 0747113	A	11-12-1996	CN 1141233 A	29-01-1997
			JP 9052030 A	25-02-1997
			US 5789081 A	04-08-1998
			US 5976433 A	02-11-1999

FR 2314215	A	07-01-1977	JP 1222318 C	15-08-1984
			JP 52094361 A	08-08-1977
			JP 58056379 B	14-12-1983
			JP 51145474 A	14-12-1976
			CA 1073822 A	18-03-1980
			DE 2625681 A	17-03-1977
			GB 1503270 A	08-03-1978
			US 4134837 A	16-01-1979

US 3907675	A	23-09-1975	FR 2201911 A	03-05-1974
			FR 2233086 A	10-01-1975
			BE 802580 A	21-01-1974
			CA 1027721 A	14-03-1978
			CH 578027 A	30-07-1976
			DE 2337069 A	07-02-1974
			ES 417081 A	01-08-1975
			GB 1420988 A	14-01-1976
			IL 42801 A	30-04-1976
			IT 994997 B	20-10-1975
			JP 49091970 A	03-09-1974
			NL 7309747 A	22-01-1974
			ZA 7304954 A	26-06-1974

JP 55122010	A	19-09-1980	NONE	
